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Stability of CL-20, TNAZ, HMX, RDX, NG, and PETN in Moist, Unsaturated Soil

Thomas F. Jenkins, Claudia Bartolini, and Thomas A. Ranney

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ABSTRACT

The stability of a number of the chemical components of energetic materials was evaluated in three moist, unsaturated soils. This study was conducted to evaluate the stability of several components of currently used energetic materials and two chemicals that may be used in future energetic material compositions in unsaturated, moist surface soils from three military training ranges. The compounds studied were nitroglycerin (NG), pentaerythritol tetranitrate (PETN), hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX), hexanitrohexaazaisowurtzitane (CL-20), and 1,3,3-trinitroazetidine (TNAZ). Three soils from military training ranges were fortified using an aqueous spiking solution and the residual concentrations were measured after 0, 1, 4, 8, 14, and 29 days at 22°C in the dark. The results indicate that the half-life of TNAZ and NG in all three test soils was less than one day, the half-life for PETN varied from 0.45 to 2.4 days, the half-life for RDX ranged from 94 to 154 days, the half-life for HMX varied from 133 to 2,310 days, and the half-life for CL-20 varied from 144 to 686 days.

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PREFACE

This report was prepared by Dr. Thomas F. Jenkins, Research Chemist, and Claudia Bartolini, Biological Sciences Technician, U.S. Army Engineer Research and Development Center (ERDC), Cold Regions Research and Engineering Laboratory (CRREL), and Thomas A. Ranney, Staff Scientist, Science and Technology Corporation, Lebanon, New Hampshire. The research described in this report was sponsored by the U.S. Army Environmental Center, Martin H. Stutz, project monitor. The authors thank Mr. Stutz and Marianne Walsh of CRREL for reviewing this report.

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THOMAS F. JENKINS, CLAUDIA BARTOLINI, AND THOMAS A. RANNEY

1 INTRODUCTION

The manufacture, loading, storage, and use of energetic materials by the U.S. Army provides avenues for environmental contamination with these materials. These energetic materials include propellants, explosives, and pyrotechnics that are used for a variety of military purposes. Compounds used by the U.S. Army in propellant formulations include ammonium perchlorate, nitrocellulose (NC), nitroglycerin (NG), 2,4-dinitrotoluene (2,4-DNT), and nitroguanidine (NQ). Explosive formulations include 2,4,6-trinitrotoluene (TNT), hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX), pentaerythritol tetranitrate (PETN), and ammonium picrate/picric acid (AP/PA). Important compounds used in pyrotechnics include white phosphorus (WP) and ammonium perchlorate. The stability of many of these compounds in the environment has been studied by Brannon, Price, and coworkers at ERDC-EL and by several researchers at CRREL.

Price and Brannon's team has utilized a stirred reactor under controlled Eh and pH conditions to investigate the stability of a number of these compounds in soil under saturated conditions. They have studied a variety of compounds to include TNT, RDX, 2,4-DNT, NG, PETN, NQ, and HMX (Brannon et al. 1997, Price et al. 1997, 1998, 2000, 2001, in prep).

At CRREL, studies were conducted in which several of these compounds were added to unsaturated surface soils using aqueous spiking solutions and the stability of these compounds investigated. The first of these studies investigated the stability of HMX, RDX, 1,3,5-trinitrobenzene (TNB), TNT, and 2,4-DNT in three uncontaminated soils at three temperatures, -15°C , 2°C , and 22°C (Grant et al. 1993). The soils were fortified with concentrations of these analytes ranging from 0.3 mg/kg for HMX to 1.33 mg/kg for RDX and studied for a period of 56 days. A second study investigated the stability of 1,3-dinitrobenzene (DNB), 2,6-dinitrotoluene (2,6-DNT), 2,4-DNT, TNT, and RDX in uncontaminated soil from

a research minefield at Fort Leonard Wood, Missouri. Soils were fortified at concentrations ranging from 0.16 mg/kg for RDX to 0.57 mg/kg for TNT and stored at -4°C , 4°C , and 22°C for periods up to 30 days (Miyares and Jenkins 2000). The results from both of these studies indicated that all of the nitroaromatic compounds (TNT, TNB, DNB, 2,4-DNT, and 2,6-DNT) were relatively unstable with half-lives ranging from a day or less in some soils for TNB and TNT to 26 days for 2,4-DNT in soils stored at 22°C . The nitramine compounds (RDX and HMX), however, were much more stable under these conditions with a measured concentration decline of 10% or less for the four soils tested over the 30- and 56-day periods studied.

Maskarinec et al. (1991) also studied the stability of HMX, RDX, TNT, and 2,4-DNT in three different soils. Maskarinec fortified his soils using an organic solvent; the addition of solvent can have an effect on the stability of at least RDX in soil under unsaturated conditions (Ringelberg et al. in press). Nevertheless, their results are in general agreement with those from the Grant and Miyares studies where the stability increases in the order $\text{TNT} < 2,4\text{-DNT} < \text{RDX} < \text{HMX}$.

Recently Ringelberg et al. (in press) conducted a similar stability study for RDX in a soil from a military training range in Alaska. Under unsaturated conditions at $21^{\circ} \pm 2^{\circ}\text{C}$, the half-life of RDX in this soil was about 29 days, somewhat shorter than found for RDX in seven other soils investigated by Grant, Miyares, and Maskarinec.

To our knowledge, no studies on the stability of NG, PETN, hexanitrohexaazaisowurtzitane (CL-20), 1,3,3-trinitroazetidine (TNAZ), NQ, or NC in unsaturated soils have been reported.

It should be emphasized that the half lives obtained for these compounds in this study pertain to the stability of the compound once it has dissolved from the solid matrix and is in intimate contact with soil and soil solution. Neither the rate of solubilization from its solid nor its kinetics of dissolution from a matrix in which it is absorbed, are included in these half lives.

2 EXPERIMENTAL METHODS

Chemicals

All standards and test solutions for NG, PETN, HMX, and RDX were prepared from Standard Analytical Reference Materials (SARMs) obtained from the U.S. Army Environmental Center (AEC), Aberdeen Proving Ground, Maryland. Standards for CL-20 and TNAZ were obtained from Steve Nicolich, Picatinny Arsenal, New Jersey. Aqueous standards and test solutions were prepared in reagent-grade water obtained from a Milli-Q Type-1 Reagent-Grade Water System (Millipore Corp.). Isopropanol (IPA) used in the preparation of HPLC eluent and the acetonitrile (AcN) used for soil extractions were HPLC-grade from Burdick and Jackson. RP-HPLC eluent was prepared by combining water and IPA at a ratio of 85/15 (v/v) and vacuum filtering through a nylon membrane (0.45 μm) to de-gas and remove particulate matter.

Analyte spiking solutions

All analyte spiking solutions were prepared in water. Standards for pentaerythritol tetranitrate (PETN), hexanitrohexaazaisowurtzitane (CL-20), nitroglycerin (NG), 1,3,5-hexahydro-1,3,5-trinitrotriazine (RDX), 1,3,5,7-octahydro-1,3,5,7-tetranitrotetrazocine (HMX), and 1,3,3-trinitroazetidine (TNAZ) were placed in individual brown glass jugs, reagent-grade water was added, and the contents were stirred at room temperature for a week. The solutions were then filtered through 0.45- μm nylon membranes into clean, brown glass jugs. No solvents, other than water, were used in the preparation of these solutions.

The concentration of analyte in each aqueous spike solution was determined against standards prepared in acetonitrile diluted 1:1 with reagent-grade water prior to analysis (EPA 1994, Jenkins et al. 1989). A multi-analyte spiking solution was prepared by combining appropriate volumes of these individual analyte solutions and filtering through a 0.45- μm nylon membrane. The combined analyte spike solution was stored in the refrigerator in a 200-mL glass flask covered with aluminum foil until used.

3 SOILS

Blank test soils were obtained from the Washington Range at Fort Greely, Alaska (FG), Yakima Training Center, Washington (YTC), and Camp Guernsey, Wyoming (CG). These soils were air-dried, ground with a mortar and pestle, and passed through a 20-mesh sieve (850 μm). Some physical and chemical properties of these soils are presented in Table 1.

Table 1. Physical and chemical properties of test soils.			
Property	Fort Greely	Yakima TC	Camp Guernsey
pH	7.2	6.2	7.7
TOC (%)	1.1	2.0	1.6
Clay (%)	3.0	20.1	25.0
CEC (meq/100g)	9.0	19.6	30.3

Replicate 5.0- \pm 0.1-g subsamples of each blank soil were placed in individual 20-mL glass scintillation vials. These samples were extracted and analyzed by RP-HPLC as described below. No target analytes were detected in these three unfortified soils.

Soil wetting and analyte spiking

Prior to the onset of the experiment, a total of 63 vials containing 5-g portions of soil for each of the three previously air-dried test soils were rewetted with 0.25 mL of reagent-grade water. After adding water, all soils were allowed to stand at room temperature in the dark for three days to allow microbiological activity to be reestablished (Maskarinec et al. 1991). This procedure has been shown to reestablish soil respiration (Grant et al. 1993).

After the three-day rest period, fortification of the three initially blank soils was made by carefully adding 1.00 mL of a spiking solution containing known concentrations of HMX, RDX, CL-20, TNAZ, NG, and PETN to each test vial using a glass volumetric pipette (Table 2). Except for the soils designated as "Day 0 exposure," the spiked soils were held at room temperature ($22^{\circ} \pm 2^{\circ}\text{C}$) in the dark. The Day 0 samples were permitted to stand for one hour after fortification to allow time for the analytes to interact with the soils prior to extraction.

Table 2. Concentration of combined analyte spiking solution and initial analyte concentrations in test soils.

	Analyte spiking solution (mg/L)	Initial concentration of spiked soil (mg/kg)
HMX	0.720	0.144
TNAZ	1.495	0.299
RDX	0.695	0.139
CL-20	1.096	0.219
NG	0.865	0.173
PETN	0.701	0.140

To test the accuracy of spike solution addition, a repeatability test was conducted. The results for this repeatability test are shown in Table 3. Aliquots of 1.00 mL of water were added to a tared vial and the weight recorded. This test showed that the mean mass spiked was 0.995 ± 0.004 g for a relative standard deviation of 0.40%.

Table 3. Repeatability test for spiked volume of solution.

Vial number	Grams
1	1.004
2	0.990
3	0.997
4	0.995
5	0.992
6	0.997
7	0.993
8	0.994
9	0.993
10	0.998
Mean	0.995
Standard deviation	0.004

Soil storage time test parameters

A summary of the test parameters used for this study is presented in Table 4. At each time period, three randomly selected vials of each type of spiked soil were selected for extraction and analysis. Only room temperature was examined ($22^{\circ} \pm 2^{\circ}\text{C}$). Samples were extracted and analyzed after 0, 1, 4, 8, 14, and 29 days of storage in the dark and the analyte concentrations determined.

Table 4. Experimental factors for soil holding time study.		
Factors	Number of levels	Levels
Analytes	6	HMX, TNAZ, RDX, CL-20, NG, PETN
Soils	3	Fort Greely, Yakima TC, Camp Guernsey
Storage temp. ($^{\circ}\text{C}$)	1	$22^{\circ} \pm 2^{\circ}\text{C}$
Storage time (days)	6	0, 1, 4, 8, 14, 29
Replicates	3	a, b, c

Soil extraction

For soil extraction, 5.00 mL of acetonitrile was added to the vials containing the soil. The vials were vortex-mixed for one minute and placed in a sonic bath for approximately 18 hours. Bath temperature was maintained at less than 25°C with cooling water. The vials were then removed from the bath and allowed to stand undisturbed for 30 minutes. A 5.0-mL aliquot of 5.0 g/L CaCl_2 aqueous solution was then added, the vials were shaken, and the soil particles were allowed to flocculate for 30 minutes before a 5.0-mL aliquot of the supernatant was removed and filtered through a 0.45- μm Millex SR filter.

This extraction procedure was based on the method developed by Jenkins et al. (1989) (SW846 Method 8330, EPA 1994) with two differences. First, the soils were not air-dried prior to extraction, because it was judged that the time required to dry the soil in the vials at room temperature could result in additional analyte loss and confound the effect of the storage time. Second, a 5.0-g portion of soil was used for the fortified samples instead of the usual 2-g sample size. This was necessary because the solubility of many of the analytes is limited (4 mg/L for HMX, for instance) as was the moisture-holding capacity of the test soils. Thus to obtain sufficiently high extract concentrations of these analytes without exceeding the moisture-holding capacity of the soils, larger soil samples were required.

RP-HPLC analysis

All soils were analyzed by reversed-phase high-performance liquid chromatography (RP-HPLC). Analysis was conducted on a modular system composed of a Spectra Systems Model SP1000 ternary HPLC pump, a Spectra Systems Spectra 2000 UV variable wavelength detector set at 210 and 254 nm (cell path 1 cm), a Spectra System AS3000 autosampler equipped with a Rheodyne Model 7125 sample loop injector, and analyzed with ChromQuest software.

All extracts were analyzed on a 3.9- × 150-mm (4-μm) LC-8 column (Nova-Pak Waters) eluted with 15:85 isopropyl alcohol/water (v/v) at 1.4 mL/min. Samples were introduced by overfilling a 100-μL sampling loop. Retention times of the analytes of interest are shown in Table 5.

Table 5. Retention times of test analytes on an LC-8 column eluted with 1.4 mL/min of 15:85 isopropyl alcohol/water (v/v).	
Compound	Retention time (min) LC-8
HMX	1.40
TNAZ	1.71
RDX	2.56
CL-20	4.20
NG	7.58
PETN	15.81

The concentrations of HMX, TNAZ, RDX, and CL-20 were estimated using absorbance measurements at the 254-nm wavelength for peaks at the proper retention time, and likewise the concentrations of NG and PETN estimated from the absorbance at the 210-nm wavelength.

Data analysis

The mean and standard deviation for each set of triplicate measurements were calculated. Suspect individual measurements were marked on the basis of extreme values of the % RSD (> 50%) and inconsistencies in the overall pattern for that compound. Each suspect value was checked for possible computation or transcription errors. Four individual extreme values (one for HMX, two for PETN, and one for CL-20) with no assignable cause were arbitrarily excluded because they produced large distortions of both means and standard deviations.

In no case was more than one datum excluded from a triplicate set. These exclusions amounted to less than 1% of the values.

The mean values at each time period were plotted as $\ln (C/C_0)$ versus t where C is the mean concentration at each time period for a given analyte in a given soil, C_0 is concentration of that analyte/soil at time 0, and t is the storage time in days. The best-fit straight line was fitted to this data and the slope computed. For a first-order rate of depletion, the slope of this line is the rate constant.

4 RESULTS AND DISCUSSION

Initial analyte concentrations

It is important to compare the Day 0 extractable analyte concentrations in the three fortified soils (Table 6) with the expected concentrations calculated from the volume used and concentrations of target analytes in the multi-analyte spiking solution (Table 2).

Table 6. Expected and determined concentrations of target analytes in Day 0 fortified soils.

Compound	Expected conc. (mg/kg)	Mean determined soil concentration and relative standard deviations					
		FG		YTC		CG	
		mean (mg/kg)	RSD (%)	mean (mg/kg)	RSD (%)	mean (mg/kg)	RSD (%)
HMX	0.144	0.162	0.4	0.147	0.4	0.154	1.0
TNAZ	0.299	0.310	3.0	0.239	1.6	0.225	4.6
RDX	0.139	0.172	1.5	0.119	0.9	0.143	0.8
CL-20	0.219	0.259	0.6	0.254	1.0	0.229	0.8
NG	0.173	0.206	2.0	0.191	4.1	0.182	1.9
PETN	0.140	0.146	4.3	0.143	2.4	0.143	4.3

The determined concentration estimates from the Day 0 analyses are shown in Table 6 along with the expected concentrations. Each of the determined values is a mean of three replicates. The relative standard deviations are less than 5% in all cases although two outlying values were rejected, one for CL-20 in FG soil and one for HMX in CG soil.

The determined concentrations for all the spiked analytes in the FG soils were always higher than for the other two soils. The soils of a given type were spiked in a batch and perhaps there was a slight bias between batches during the spiking activity. This could account for the relatively small, but consistent, differences observed for HMX, CL-20, NG, and PETN. The difference for TNAZ may be due to a more rapid loss of TNAZ in the CG and YTC soils compared to the FG soil during the one-hour period that the Day 0 samples were held after spiking and before extraction. As will be seen later, the loss of TNAZ in all three

Table 8. Concentrations of analytes as a function of holding time, Yakima Training Center (YTC) soil.

Compound	Mean concentration (mg/kg) \pm standard deviation (mg/kg)											
	Holding time											
	0 days		01 day		04 days		08 days		14 days		29 days	
	X	S	X	S	X	S	X	S	X	S	X	S
HMX	0.147	0.001	0.149	0.002	0.149	0.001	0.150	0.007	0.145	0.001	0.138	0.003
TNAZ	0.239	0.004	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
RDX	0.119	0.001	0.123	0.002	0.117	0.002	0.116	0.002	0.107	0.001	0.107	0.001
CL-20	0.254	0.003	0.254	0.004	0.227	0.003	0.230	0.003	0.231	0.001	0.231	0.005
NG	0.191	0.008	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
PETN	0.143	0.003	0.087	0.005	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000

Table 9. Concentrations of analytes as a function of holding time, Camp Guernsey (CG) soil.

Compound	Mean concentration (mg/kg) \pm standard deviation (mg/kg)											
	Holding time											
	0 days		01 day		04 days		08 days		14 days		29 days	
	X	S	X	S	X	S	X	S	X	S	X	S
HMX	0.154	0.002	0.158	0.001	0.155	0.003	0.152	0.004	0.150	0.002	0.147	0.002
TNAZ	0.225	0.010	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
RDX	0.143	0.001	0.150	0.001	0.135	0.000	0.137	0.005	0.128	0.002	0.117	0.008
CL-20	0.229	0.002	0.231	0.002	0.216	0.005	0.224	0.006	0.225	0.003	0.212	0.007
NG	0.182	0.003	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
PETN	0.143	0.006	0.031	0.001	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000

The stability of PETN in these fortified soils is slightly greater than TNAZ or NG. At room temperature, an average 75% remained after one day in the FG soil, 61% in the YTC soil, and 22% in CG soil. After four days, PETN had disappeared in all of the soils. The rate of loss of PETN appears to vary from soil to soil in the following order: CG > YTC > FG. The above pattern for the rate of loss in the different soils correlates with the clay content of these soils, the clay content of the FG soil being much lower than that of the other two soils (Table 1).

The stability of HMX, RDX, and CL-20 in these three fortified unsaturated soils is much greater than that of TNAZ, nitroglycerin, or PETN. The stability of HMX and RDX in unsaturated soils is in agreement with that found elsewhere that indicated that RDX and HMX were quite stable in the environment under aerobic conditions (Hoffsommer et al. 1978, Spanggord et al. 1980, Grant et al.

1993, Miyares and Jenkins 2000, and Ringelberg et al. in press). The overall mean recoveries for HMX after 29 days were 95% for the CG, 85% for FG, and 97% for YTC soils. Likewise for RDX, the mean recoveries were 82% for the CG soil, 81% for FG, and 90% for YTC. For CL-20 the mean recoveries after 29 days were 93% for CG, 76% for FG, and 91% for YTC. To date, CL-20 has not been studied extensively because it is a newly developed explosive. Its stability, however, appears to be quite similar to RDX and HMX.

To investigate the rate of loss and estimate the half-lives of these explosives, the mean concentrations obtained at each time period were plotted as the $\ln(C/C_0)$ versus time (t), where C is the concentration at time t and C_0 is the initial concentration at time 0 (Fig. 1–3). For a first-order rate process, a linear relationship should be obtained. If a process is first order, the half-life can be determined easily using the simple rate equation

$$\ln(C/C_0) = -kt \quad (1)$$

where k is the rate constant equal to the slope of the relationship. The half-life is then calculated by dividing the natural logarithm (\ln) of C/C_0 where C/C_0 is 0.5 (-0.693) by the first-order rate constant. An important point to note is that when the rate is first order, the half-life is independent of the starting concentration.

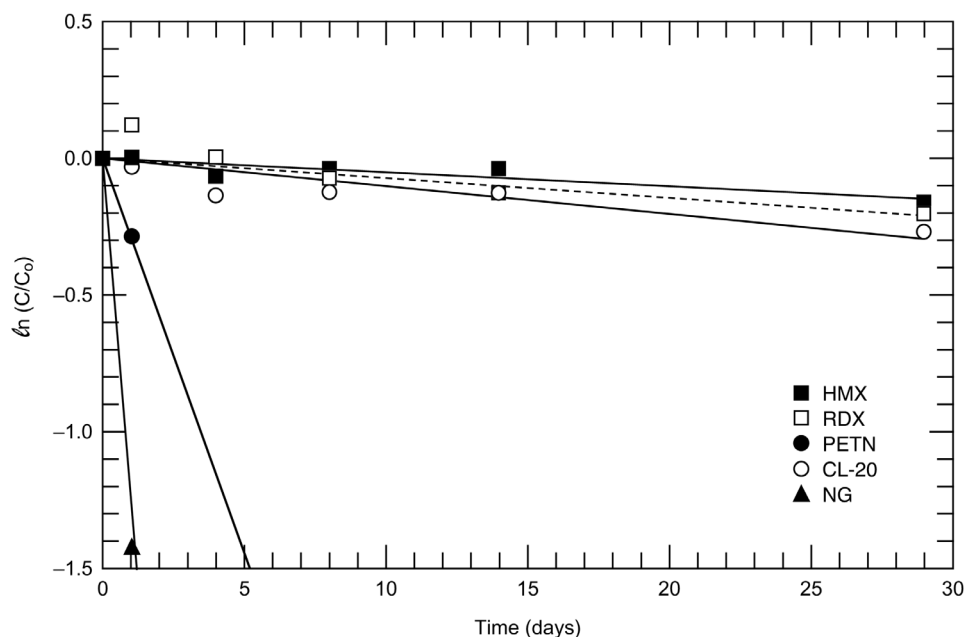


Figure 1. Analyte loss with time in Fort Greely soil.

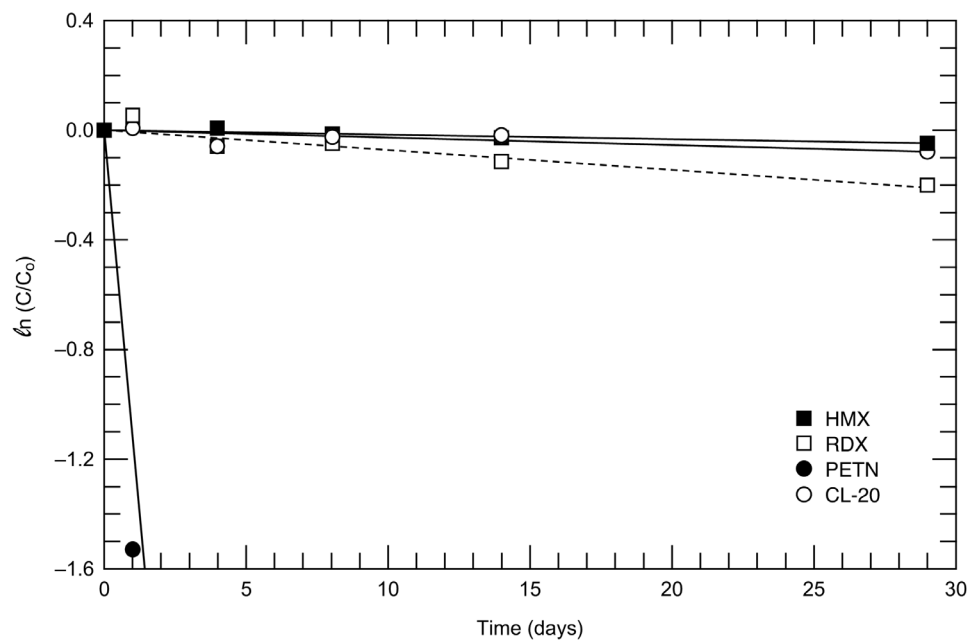


Figure 2. Analyte loss with time in Camp Guernsey soil.

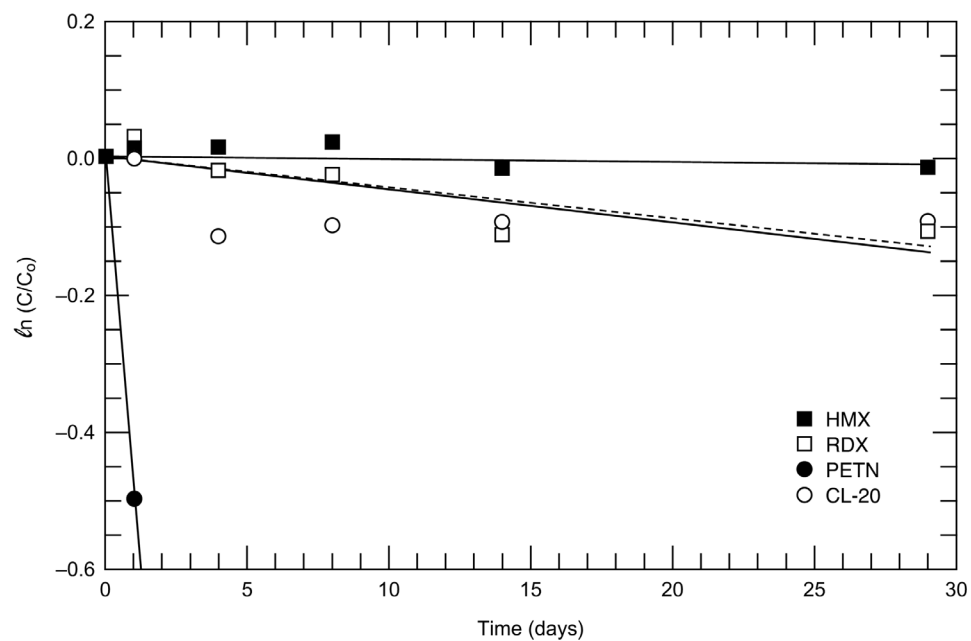


Figure 3. Analyte loss with time in Yakima Training Center soil.

It appears that rate of disappearance of HMX and RDX follows first-order kinetics. It is not possible to determine if the loss of TNAZ is first order because the rate of loss is so great that concentrations of TNAZ were below analytical detection limits after only one day for all three soils. This is also true for NG where residual concentrations were observed at Day 1 for only one of the three soils. For PETN, residual concentrations were observed for Day 1, but the concentrations had declined below analytical detection limits in all of the three soils by Day 4 and hence there is insufficient data to evaluate whether its loss follows first-order kinetics. For purposes of half-life computation, the loss of TNAZ, NG, and PETN was assumed to follow first-order kinetics.

The half-lives calculated from the first-order rate constants for RDX for the three soils varied from 94 days for the FG soil to 154 days for the YTC soil (Table 10). Similarly, half-life estimates for HMX and CL-20 varied from 133 to 2,310 days and 144 to 686 days, respectively. The half-life estimate for PETN varied from 0.45 to 2.4 days. The half-life estimates for TNAZ and NG were less than one day for all three test soils.

Table 10. Half-life estimates (days) in three test soils.			
Analyte	FG	CG	YTC
HMX	133	433	2310
TNAZ	<1	<1	<1
RDX	94	98	154
CL-20	69	267	144
NG	0.49	<1	<1
PETN	2.4	0.45	1.4

5 CONCLUSIONS

The stability discussed in this study refers to the stability of these compounds in soil after they have dissolved from particles and have equilibrated between soil solution and soil surfaces. For example, the stabilities reported here do not include the kinetics of dissolution of NG from particles of double-based or triple-based propellants. Thus, chemical analysis of surface soils at firing points may indicate that NG is present for long periods after a firing event, but this NG is likely still imbibed within the nitrocellulose matrix and is not in contact with the soil. Once dissolved from the matrix, however, the very short half-life of NG reported here indicates that NG will not be sufficiently stable to leach or present a groundwater contamination problem.

Similarly, TNAZ and PETN have very short half-lives in soil and should not present a ground-water contamination problem either. CL-20, on the other hand, has a long half-life in soil, ranging from 144 to 686 days in these three test soils. It is only slightly soluble in water, but once dissolved, it will probably behave similarly to RDX and HMX.

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14. ABSTRACT The stability of a number of the chemical components of energetic materials was evaluated in three moist, unsaturated soils. This study was conducted to evaluate the stability of several components of currently used energetic materials and two chemicals that may be used in future energetic material compositions in unsaturated, moist surface soils from three military training ranges. The compounds studied were nitro-glycerin (NG), pentaerythritol tetranitrate (PETN), hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX), hexanitrohexaazaisowurtzitane (CL-20), and 1,3,3-trinitroazetidine (TNAZ). Three soils from military training ranges were fortified using an aqueous spiking solution and the residual concentrations were measured after 0, 1, 4, 8, 14, and 29 days at 22°C in the dark. The results indicate that the half-life of TNAZ and NG in all three test soils was less than one day, the half-life for PETN varied from 0.45 to 2.4 days, the half-life for RDX ranged from 94 to 154 days, the half-life for HMX varied from 133 to 2,310 days, and the half-life for CL-20 varied from 144 to 686 days.					
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